

6.3 Electrical conductivity

6.3.1 Scope and application

This method measures the electrical conductivity (EC) of a 1:5 soil–water suspension. Electrical conductivity of the soil is sometimes used to estimate the soluble salt content of a sample (Rayment & Higginson 1992, p.17). A high soluble salt content may have physical detrimental effects on a soil, compromising its agronomic and structural attributes, for example, increasing potential for corrosion of below-ground structures.

The same 1:5 soil–water suspension for pH determination may be used for measuring the electrical conductivity but to avoid contamination, electrical conductivity should be analysed first.

6.3.2 Principle

The electrical conductivity is measured on the aqueous extract of a 1:5 soil–water suspension and recorded in dS/m at 25°C.

6.4 Cation exchange capacity and exchangeable cations

6.4.1 Scope and application

Methods in the following table measure the cation exchange capacity (CEC) of major exchangeable cations/‘bases’ (Ca^{2+} , Mg^{2+} , Na^+ and K^+) of near-neutral and alkaline soils.

Soil type	pH	Extractant	Salt content*	Method **	Comments
Non-calcareous & non-gypsiferous soils	7.0	1M ammonium chloride	EC < 0.3 dS/m	15B1	No pre-treatment for soluble salts
			EC > 0.3 dS/m	15B2	
			* Based on EC determined on a 1:5 soil–water extract.	15B3	
				** Soil Chemical Methods	Adjustment: corrected for soluble Na^+ when NaCl is the dominant soluble salt.

Limitation: These methods are designed to assess the ion-exchange characteristics of soils for land surveys or soil fertility studies, not contaminated soil; they should only be used with natural soils or background samples to give supporting information about the extent of contamination. In other samples the methods are qualitative and the results will be indicators only. Soils heavily contaminated with soluble metals may saturate an extractant’s exchangeable sites and may not, by itself, provide a true indication of the soil’s exchangeable capacity.

US EPA Method 9081 (US EPA SW-846) can be used on most soils (calcareous and non-calcareous) to measure the total amount of displaced ions from exchangeable sites in soil, compared with the summation of individual ions to express the soil’s CEC.

6.4.2 Principle

The soil is shaken with an appropriate extractant under certain conditions to exchange cations in the soil with the chosen extracting ions. The processed extract is then analysed for exchangeable cations including Na⁺, K⁺, Ca²⁺ and Mg²⁺, or total CEC.

6.5 Water-soluble chloride

6.5.1 Scope and application

This method measures water-soluble chloride in soil water extracts (1:5 soil–water) (Rayment & Higginson 1992, p.24–25).

6.5.2 Principle

Chloride in soil is extracted in deionised water and the chloride concentration determined by colorimetric analysis or potentiometric titration.

6.5.3 Interferences

Water-soluble colour in the soil may mask the colour change at the endpoint of the titration. If this occurs, the colour can be removed by adding an aluminium hydroxide suspension (APHA Method 4500-Cl). Alternatively, chloride in the water extract can be determined using an ion-selective electrode or ion-chromatography.

6.6 Organic carbon

6.6.1 Scope and application

This determination (Rayment & Higginson 1992, p. 29), also known as the Walkley & Black method, measures the oxidisable organic carbon content of soils and may also be used to estimate their total organic carbon (TOC) content.

Soil organic carbon comprises a variety of carbonaceous materials including humus, plant and animal residues, microorganisms, coal, charcoal and graphite. It does not include carbonate minerals such as calcite or dolomite. Australian soils generally contain less than 5% organic carbon, with higher levels common in surface soils (Rayment & Higginson 1992, p. 29 and p. 32).

The first method listed in Rayment gives poor recoveries of carbonised materials such as graphite, coal, coke and similar coal derivatives. If such materials make up the bulk of the carbon in the sample or if the total organic carbon content is required, an alternative method, which makes use of an external heat source, is recommended (Rayment & Higginson 1992, p. 32).

For organic carbon analysis in acid sulfate soils, consult the Australian standard for the *Analysis of acid sulfate soil—dried samples—methods of test—introduction and definitions, symbols and acronyms*, (AS 4969.0-2008) for relevant definitions and recommended analytical procedures.

6.6.2 Interferences

Overestimation of organic carbon may occur due to large amounts of chloride or metallic or ferrous iron in the sample. Underestimation may result when large amounts of higher oxides of manganese are present. These interferences are common in Australian soils. The potential interferences should be taken into account, particularly when analysing some types of poorly aerated soils.

Since the first method recovers variable proportions of organic carbon actually present in a soil sample (recoveries typically in the range of 65–85%), a correction factor is usually needed. In the absence of a specific correction factor for the soil being tested, a correction factor of 1.3 is commonly used such that:

$$\text{Total organic carbon (\%)} = \text{Oxidisable organic carbon (\%)} \times 1.3$$

7 Metals

7.1 Aqua regia digestible metals

7.1.1 Scope and application

Method AS 4479.2-1997 may be used to obtain extracts from soils for the analysis of most metals and metalloids. Extracts obtained here are not suitable for speciation studies, and analysis of the extracts does not necessarily result in total or bioavailable heavy metal levels in a soil.

Metals extractable by this digestion include metallic components adsorbed on soil particles, complexed by and adsorbed on organic matter, and soluble metal salts. Complete decomposition of the soil is not possible using aqua regia; therefore metals bound within part or most of the silicate matrix may not be fully recovered by this method.

Samples extracted by this method can be analysed for metals by a suitable spectrophotometric method, while accounting for likely interferences, for example, chlorides.

US EPA SW-846 Method 3050B, SW-846 Method 3051A (microwave-assisted digestion) or Method 200.2 may be used as alternatives to this method.

7.1.2 Principle

Boiling aqua regia (3:1 hydrochloric/nitric acid) is used to extract metals from soil. This concentrated acid mixture can extract inorganic metals as well as those bound in organic or sulfide forms.

7.2 Acid digestible metals in sediments, sludges and soils

7.2.1 Scope and application

This method (US EPA SW-846, Method 3050B) may be used to prepare extracts from sediments, sludges and soils for the analysis of metals by various common spectrophotometric techniques.

It can be used to determine the following extracted metals:

FAAS/ICP-AES		GFAAS/ICP-MS
Aluminium	Magnesium	Arsenic
Antimony	Manganese	Beryllium
Barium	Molybdenum	Cadmium
Beryllium	Nickel	Chromium
Cadmium	Potassium	Cobalt
Calcium	Silver	Iron
Chromium	Sodium	Lead
Cobalt	Thallium	Molybdenum
Copper	Vanadium	Selenium
Iron	Zinc	Thallium
Lead		

FAAS	=	Flame atomic absorption spectroscopy
GFAAS	=	Graphite furnace atomic absorption spectroscopy
ICP-AES	=	Inductively coupled plasma atomic emission spectroscopy
ICP-MS	=	Inductively coupled plasma mass spectrometry

7.2.2 Principle

Two separate digestion procedures, whose extracts are not interchangeable for each other's determinations, are provided for determination of the above elements.

7.2.2.1 For FAAS and ICP–AES

The field-moist or dry sample is digested at 95°C in nitric acid and hydrogen peroxide until the volume is reduced, or heated for two hours. Hydrochloric acid is then added and the mixture digested further at heat.

For improved solubility and recovery of antimony, barium, lead and silver, an optional nitric acid/hydrochloric acid digestion step may be used when necessary.

7.2.2.2 For GFAAS and ICP–MS

The field-moist or dry sample is digested at 95°C in nitric acid and hydrogen peroxide until the volume is reduced, or heated for two hours.

7.3 Metals by microwave assisted acid digestion of sediments, sludges, soils and oils

7.3.1 Scope and application

This method (US EPA SW-846, Method 3051A) describes a rapid acid-assisted microwave procedure for digesting sediments, sludges, soils and oils for the analysis of most metals, some metalloids and some non-metals, including (but not limited to):

Aluminium	Cadmium	Iron	Molybdenum	Sodium
Antimony	Calcium	Lead	Nickel	Strontium
Arsenic	Chromium	Magnesium	Potassium	Thallium
Barium	Cobalt	Manganese	Selenium	Vanadium
Boron	Copper	Mercury	Silver	Zinc
Beryllium				

7.3.2 Principle

The sample is digested in concentrated nitric acid, or a mixture of nitric and hydrochloric acids, using microwave heating in a sealed Teflon™ vessel at elevated temperature and pressure. The final digest can be analysed for the element by various common spectrophotometric methods, as described in US EPA Method 3051A.

7.4 Mercury

7.4.1 Scope and application

This method (US EPA SW-846, Method 7471B) may be used as an alternative to methods described in this Schedule for mercury. It uses strong acid digestion (aqua regia) to determine total mercury (inorganic and organic) in soils, sediments, bottom deposits and sludge-type materials.

7.4.2 Principle

Mercury is digested with aqua regia (1:3 nitric acid/hydrochloric acid) at 95°C in the presence of a strong oxidant (potassium permanganate). The digest is then analysed by cold-vapour atomic absorption spectrometry.

CAUTION: Mercury vapour is highly toxic. Use appropriate safety precautions ensuring the mercury vapour is vented into an appropriate exhaust hood or, preferably, trapped in an absorbing medium (e.g. potassium permanganate/sulfuric acid solution).

Note: US EPA Method 1630 may be used for methyl mercury.

7.5 Hexavalent Chromium

7.5.1 Scope and application

This method (US EPA SW-846, Method 3060A) is an alkaline digestion procedure for extracting hexavalent chromium [Cr (VI)] from soluble, adsorbed and precipitated forms of chromium compounds in soils, sludges, sediments and similar waste materials.

7.5.2 Principle

The method uses an alkaline digestion to solubilise both water-soluble and water-insoluble Cr(VI) compounds. The pH should be carefully monitored during digestion to prevent reduction of Cr(VI) or oxidation of native Cr(III).

Cr(VI) in the digest can then be determined colourimetrically by UV visible spectrophotometry (US EPA SW-846, Method 7196), ion chromatography (US EPA SW-846, Method 7199) or other suitable validated methods.

CAUTION: Cr(VI) is highly toxic. Use appropriate safety precautions when handling and disposing of waste.

8 Halides

8.1 Bromide

8.1.1 Scope and application

This method (Adriano & Diner 1982, p. 449) is applicable to the determination of water-soluble bromides in soils, sediments and other solids.

8.1.2 Principle

Most bromides in soils are considerably soluble and can be readily leached using water. In this method, bromide in the sample is extracted into water with a suitable soil:water ratio, which will depend on the bromide species and concentration present. Determination is by suitable APHA methods (APHA Methods 4500-Br and 4110).

8.2 Fluoride

8.2.1 Scope and application

This method is applicable to the determination of total fluoride in plants, soils, sediments and other solids (ASTM D3269-96 (2001), McQuaker & Gurney 1977, ASTM D3270-00 (2006)).

8.2.2 Principle

The sample is fused with sodium hydroxide at 600°C and a solution of the melt is analysed for fluoride.

Note 1: To avoid fluoride losses, do not use glassware to hold sample extracts for long periods; use plasticware as far as possible.

Note 2: This method is not appropriate for samples with high aluminium concentrations, which can cause negative interferences.

Bromomethane	Dichlorodifluoromethane	Tetrachloroethene
Carbon tetrachloride	Dichlorethanes	Trichlorobenzenes
Chlorobenzene	Dichlorethene	Trichloroethanes
Chlorodibromomethane	Dichloromethane (methylene chloride)	Trichloroethene
Chloroethane	1,2-Dichloropropane	Trichlorofluoromethane
2-Chloroethanol	1,3-Dichloro-2-propanol	Trichloropropanes
2-Chloroethyl vinyl ether	1,3-Dichloropropene	Vinyl chloride
Chloroform		

10.1.3.1 Sample extraction

Low concentration (<200 µg/kg, for individual compounds):

- purge and trap technique (Method 5035, Method 5030B)

Analysts should determine an appropriate concentration limit and ensure that results are based on sample concentrations that do not exceed the instrument range.

High concentration (≥200 µg/kg, for individual compounds):

- methanol extraction followed by purge and trap technique (Method 5035 or 5030B).

10.1.3.2 Sample clean-up

Not applicable.

10.1.3.3 Sample analysis

The table below lists the US EPA SW-846 methods specified for volatile halogenated compounds.

8021B	GC/ELCD
8260B	GC/MS

Note: Preliminary screening by headspace analysis (Method 5021) or hexadecane extraction (Method 3820) is appropriate for samples that may contain high concentrations.

10.1.4 Miscellaneous volatile organic compounds

The following volatile compounds do not fall into the aromatic or chlorinated categories detailed in the sections above, and may be analysed using the methods below.

10.1.4.1 Scope

Analysis of other volatile organics by these methods is not precluded. These methods could also be appropriate for volatile petroleum products (hydrocarbon fuels and solvents).

Acetone	Ethyl methacrylate
Acetonitrile	2-Hexanone
Acrolein	2-Hydroxypropionitrile
Acrylonitrile	Isobutyl alcohol
Allyl alcohol	Light alkanes (e.g. as in petrol)
2-Butanone (MEK)	Malononitrile
t-Butyl alcohol	Methacrylonitrile
Carbon disulfide	Methyl methacrylate
Chloral hydrate	4-Methyl-2-pentanone (MIBK)
bis-(2-Chloroethyl) sulphide	2-Picoline
2-Chloroethyl vinyl ether	Propargyl alcohol
1,2:3,4-Diepoxybutane	b-Propiolactone

Diethyl ether
 1,4-Dioxane
 Ethanol
 Ethylene oxide

Propionitrile
 n-Propylamine
 Pyridine
 Vinyl acetate

10.1.4.2 *Sample extraction*

Low concentration (<200 µg /kg, for individual compounds):

- purge and trap technique (Method 5035)

Analysts should determine an appropriate concentration limit and ensure that results are based on sample concentrations that do not exceed the instrumental range.

High concentration (≥200 µg/kg, individual compounds):

- methanol extraction followed by purge and trap technique.

10.1.4.3 *Sample clean-up*

Not applicable.

10.1.4.4 *Sample analysis*

The table below lists the specified US EPA SW-846 method.

8260B	GC/MS
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10.1.5 Total recoverable hydrocarbons - volatile

The term ‘TRH’ (total recoverable hydrocarbons) is equivalent to the previously used term ‘TPH’ (total petroleum hydrocarbons), and represents extracted biogenic and petrogenic (petroleum) hydrocarbons by selected solvents. The new terminology has been chosen to avoid confusion with past practices.

TRH fractions are based on newly derived health screening levels (HSL) for petroleum hydrocarbon products.

The vTRH method is applicable but not limited to analysis of volatile hydrocarbons which may be constituents or residues present in or from materials such as the following:

- petrol
- dry cleaning liquids
- industrial solvents
- paints, thinners and strippers.

10.1.5.1 *Scope*

This method, which is a modified version of the ‘closed-system purge and trap and extraction for volatile organics in soil and waste samples method’ (Method 5035), is applicable to hydrocarbons eluting between nC₆ and nC₁₀. A clean-up procedure is not applicable here since only the volatile components are being investigated.

10.1.5.2 *Sample extraction*

The table below lists the specified US EPA SW-846 method.

5035	Purge and trap extraction using methanol
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10.1.5.3 Extract clean-up

Not required/applicable.

10.1.5.4 Extract analysis

The table below lists the specified US EPA SW-846 method.

8260B	GC/MS or GC/FID. Volatile TRH fraction is specified as nC ₆ -nC ₁₀ . Details of GC conditions, standards, and procedure for quantification of fractions as suggested by CRC CARE are listed in Appendix 1.
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10.2 Semi-volatile organics

10.2.1 Scope and application

This section lists methods for the following classes of non-volatile compounds:

- non-volatile chlorinated hydrocarbons
- PAHs by solvent extraction
- PAHs by supercritical fluid extraction
- organochlorine pesticides (OCPs) and PCBs
- OPPs
- total recoverable hydrocarbons – non-volatile
- phenols
- chlorinated herbicides
- phthalate esters
- dioxins and furans.

Note: Many of these methods use ultrasonic extraction. When this method is used, ensure samples do not overheat; consider putting ice packs into the ultrasonic bath.

This method should not be used for volatile contaminants.

10.2.2 Semi-volatile chlorinated hydrocarbons

This method is applicable but not limited to the analysis of the following semi-volatile chlorinated hydrocarbons.

Benzal chloride	Benzotrichloride
Benzyl chloride	2-Chloronaphthalene
Dichlorobenzenes	Trichlorobenzenes
Tetrachlorobenzenes	Pentachlorobenzenes
Hexachlorobenzene	Hexachlorobutadiene
Hexachlorocyclopentadiene	Hexachloroethane
Hexachlorocyclohexane (alpha-HCH)	Hexachlorocyclohexane (beta-HCH)
Hexachlorocyclohexane (gamma-HCH or Lindane)	Hexachlorocyclohexane (delta-HCH)

10.2.2.1 Sample extraction

The table below lists the specified US EPA SW-846 methods.

3540C	Soxhlet extraction using: acetone/hexane (1:1) or dichloromethane/acetone (1:1)
3550C	<p>Ultrasonic extraction* using:</p> <p>a. for low concentration (individual compounds <20 mg/kg): dichloromethane or dichloromethane/acetone (1:1) or hexane/acetone (1:1) or methyl tertiary-butyl ether or methyl tertiary-butyl ether/methanol (2:1).</p> <p>The solvent system chosen should be shown to give optimum, reproducible recovery of analytes spiked into the particular matrix (soil type) under test. Analysts should determine an appropriate concentration limit and ensure that quantitative results are based on sample concentrations that do not exceed the instrument range.</p> <p>b. for high concentration (individual compounds >20 mg/kg): dichloromethane or hexane</p>

* Ensure samples do not overheat.

3545A	Pressurised fluid extraction
CRC CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking

10.2.2.2 *Extract clean-up*

3620C	Florisil® column clean-up or
3640A	Gel permeation column clean-up and
3660B	Sulfur clean-up if necessary.

10.2.2.3 *Extract analysis*

	8121	GC/ECD
(P)	8270D	GC/MS

10.2.3 Polycyclic aromatic hydrocarbons by solvent extraction

10.2.3.1 *Scope and application*

This method is applicable but not limited to analysis of the following polycyclic aromatic hydrocarbons (PAHs):

Naphthalene
 Acenaphthylene
 Acenaphthene
 Fluorene
 Phenanthrene
 Benzo(b)fluoranthene

Anthracene
 Fluoranthene
 Pyrene
 Benzo(a)anthracene
 Chrysene

Benzo(k)fluoranthene
 Benzo(a)pyrene
 Dibenz(a,h)anthracene
 Benzo(ghi)perylene
 Indeno(123-cd)pyrene

10.2.3.2 *Sample extraction*

The tables below list the specified US EPA SW-846 methods.

3540 C	Soxhlet extraction using: acetone/hexane (1:1) or dichloromethane/acetone (1:1)
3550 C	<p>Ultrasonic extraction* using:</p> <p>a. for low concentration (individual compounds <20 mg/kg): dichloromethane or dichloromethane/acetone (1:1) or hexane/acetone (1:1) or methyl tertiary-butyl ether or methyl tertiary-butyl ether/methanol (2:1).</p> <p>The solvent system chosen should be shown to give satisfactory, reproducible recovery of analytes spiked into the particular matrix (soil type) under test.</p> <p>Analysts should determine an appropriate concentration limit and ensure that results are based on sample concentrations that do not exceed the instrument range.</p> <p>b. for high concentration (individual compounds >20 mg/kg): dichloromethane.</p>

* Ensure samples do not overheat.

3545A CRC CARE TPH TECHNICAL WORKING GROUP	Pressurised fluid extraction using dichloromethane/acetone (1:1). End-over-end tumbling/shaking
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10.2.3.3 *Sample clean-up*

3630C	Silica gel column clean-up
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The extract should be concentrated using a Kuderna Danish (KD) evaporator or other suitable method and solvent exchanged to cyclohexane, prior to clean-up.

10.2.3.4 *Extract analysis*

(P)	8270D	GC/MS (capillary column)
	8310	HPLC with UV* and fluorescence* detectors

*Due to the high probability of interferences using these less specific detectors, clean-up of extracts using Method 3630C will normally be necessary. Protocols for verification of analyte identities should be developed when Method 8310 is used.

10.2.4 Polycyclic aromatic hydrocarbons by supercritical fluid extraction
PAHs / supercritical fluid extraction (SFE)

3561	SFE of PAHs
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10.2.4.1 *Sample extraction*

The tables below list the specified US EPA SW-846 methods. The extraction is a three-step process using:

- supercritical CO₂
- supercritical CO₂ plus water and methanol modifiers
- supercritical CO₂ (to purge system of modifiers).

Collection of SFE extract:

either

- octadecylsilyl (ODS) trap with elution of trap using:
 - a. acetonitrile/tetrahydrofuran (50/50) for HPLC determination, or
 - b. DCM (dichloromethane)/isooctane (75/25)

or

solvent trapping in solvent system (a) or (b) above, or another system validated by the laboratory.

10.2.4.2 *Extract clean-up*

The table below lists the specified US EPA SW-846 methods.

3620C	Florisil® column clean-up or
3640A	gel permeation column clean-up and
3660B	sulfur clean-up if necessary

10.2.4.3 *Extract analysis*

The table below lists the specified US EPA SW-846 methods.

(P)	8270D	GC/MS
	8310	HPLC with UV and Fluorescence detectors

10.2.5 Organochlorine pesticides and polychlorinated biphenyls

10.2.5.1 Scope and application

This method is applicable but not limited to analysis of the following organochlorine pesticides: (OCPs) and polychlorinated biphenyls (PCBs):

Aldrin	Endrin
HCB	Endosulfan (alpha-, beta- and sulfate)
alpha-HCH, beta-HCH	Heptachlor, Heptachlor epoxide
gamma-HCH (lindane), delta-HCH	Mirex
Chlordane (alpha, beta chlordane and oxychlordane)	Methoxychlor
DDD, DDE, DDT	Toxaphene
Dieldrin	PCBs (Aroclor 1016, 1221, 1232, 1242, 1248, 1254, 1260, 1262).

10.2.5.2 Sample extraction

The table below lists the specified US EPA SW-846 methods.

3540C	Soxhlet extraction using: acetone/hexane (1:1) or dichloromethane/acetone (1:1).
3550C	Ultrasonic extraction* using: a. for low concentration (individual compounds <20 mg/kg): dichloromethane or dichloromethane/acetone (1:1) or hexane/acetone (1:1) or methyl tertiary-butyl ether or methyl tertiary-butyl ether/methanol (2:1). The solvent system should be chosen to give optimum reproducible recovery of analytes spiked into the matrix (soil type) under test. Analysts should determine an appropriate concentration limit and ensure that quantitative results are based on sample concentrations that do not exceed the instrumental range. b. for high concentration (individual compounds >20 mg/kg): dichloromethane or hexane
CRC CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking

* Ensure samples do not overheat.

Note: Extract clean-up. Methods for the clean-up of some co-extracts/analytes are suggested below. The tables below list the specified US EPA SW-846 methods.

For samples of biological origin or containing high molecular weight materials:

3640A	Gel permeation column clean-up
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If only PCBs are to be determined:

3665A	sulfuric acid/permanganate clean-up followed by:
3620C	Florisol® column clean-up or
3630C	silica gel fractionation.

If both PCBs and pesticides are to be measured:

3630C	silica gel fractionation
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If only pesticides are to be determined:

3620C	Florisol® column clean-up and
3660B	sulfur clean-up.

Elemental sulfur may interfere with determination of pesticide and PCBs. This should be removed using Method 3660B: sulfur clean-up, which uses reaction with reactive copper.

10.2.5.3 Extract analysis

The table below lists the specified US EPA SW-846 methods.

8081B	GC/ECD (capillary column)
8082A	GC/ECD or GC/ ELCD
8270D	GC/MS (capillary column)

10.2.6 Organophosphorus pesticides

10.2.6.1 Scope and application

This method is applicable but not limited to the analysis of the following organophosphorus pesticides (OPPs):

Atrazine	EPN	Parathion ethyl
Azinphos methyl	Ethoprop	Parathion methyl
Bolstar (Sulprophos)	Fensulfothion	Phorate
Chlorpyrifos	Fenthion	Ronnel
Coumaphos	Malathion	Sulfotep
Demeton, O and S	Merphos	TEPP
Diazinon	Mevinphos	Stirophos (Tetrachlorvinphos)
Dichlorvos	Monocrotophos	Tokuthion (Protothiophos)
Dimethoate	Naled	Trichloronate
Disulfoton.		

10.2.6.2 Sample extraction

The table below lists the specified US EPA SW-846 methods.

3540C	Soxhlet extraction using: acetone/hexane (1:1) or
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	dichloromethane/acetone (1:1).
3550C	<p>Ultrasonic extraction* using:</p> <p>a. for low concentration (individual compounds <20 mg/kg): dichloromethane or dichloromethane/acetone (1:1) or hexane/acetone (1:1) or methyl tertiary-butyl ether or methyl tertiary-butyl ether/methanol (2:1).</p> <p>The solvent system chosen should be shown to give satisfactory, reproducible recovery of analytes spiked into the particular matrix (soil type) under test.</p> <p>Analysts should determine an appropriate concentration limit and ensure that quantitative results are based on sample concentrations that do not exceed the instrumental range.</p> <p>b. for high concentration (individual compounds >20 mg/kg): dichloromethane or hexane.</p>
CRC CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking

* Ensure samples do not overheat

10.2.6.3 Extract clean-up

This step is not usually necessary. The tables below list the specified US EPA SW-846 methods.

3620C	Florisol® column clean-up. (Analyst should verify the use of this step for the pesticide of interest, as low recoveries have been reported for certain OPPs.)
3660B	Sulfur clean-up

10.2.6.4 Sample Analysis

8141B	GC/ FPD or GC/ NPD
8270D	GC/MS

10.2.7 Total recoverable hydrocarbons

The term total recoverable hydrocarbons (TRH) is equivalent to the previously used total petroleum hydrocarbons (TPH), and represents extracted biogenic (biological) and petrogenic (petroleum) hydrocarbons by selected solvents. The term has been chosen to avoid confusion with past practices. Where significant levels of non-petroleum hydrocarbon interferences are suspected, a silica gel clean-up is recommended, in which case the analytical report should include a clear statement about this and any relevant interpretation of the chromatogram; the analysis should be referred to as 'TRH-silica'. See Section 11.2.8.1.

When soil contains high levels of non-petroleum-based hydrocarbons (e.g. from heavy manure, compost additions or polymeric materials), inspection of the TRH–silica chromatogram may reveal that the silica gel clean-up was not sufficient to remove the non-petroleum-based hydrocarbons from the sample and resolve interferences. This can result in false positive results for petroleum-based hydrocarbon determination. In these cases it is recommended that GC–MS—or other appropriate analytical method, e.g. nuclear magnetic resonance (NMR)—is applied to the extract or a silica gel cleaned sample to improve accuracy.

The analyst should discuss any unusual profiles—and the possibility of interferences from high biogenic hydrocarbon—with the site assessor, before issuing the report.

Where it can be determined that compounds in the sample are of non-petroleum origin, the results should be adjusted as far as practicable to finalise the level of petroleum-based hydrocarbon in the sample.

TRH fractions are based on those used to derive the Health Screening Levels (HSLs) for petroleum hydrocarbon compounds (See Schedule B1).

The TRH method is applicable but not limited to the analysis of hydrocarbons that may be constituents or residues present in or from materials such as the following:

- kerosene
- diesel
- aviation fuel
- lubricating oil
- heating oil/marine fuel
- dry cleaning liquids
- tars
- gasworks wastes
- industrial solvents
- paints, thinners and strippers.

10.2.8 Total recoverable hydrocarbons by solvent extraction

10.2.8.1 Scope

This method is for the determination of semi-volatile TRH in soil by gas chromatography applicable to hydrocarbons eluting between $>nC_{10}$ and nC_{40} . The method extracts major hydrocarbons such as aliphatic linear, branched and cyclic hydrocarbons, PAHs, and other compounds in the boiling point range up to nC_{40} . If PAHs are suspected of being present in a sample, target analysis techniques are preferred for risk assessments.

Hydrocarbons with boiling points less than nC_{10} (volatiles) or greater than nC_{40} (heavy petroleum compounds) will not be quantitatively determined using this method.

TRH can be defined as those compounds that are extractable into the solvent and elute from a GC column under the conditions specified in the test method. Hydrocarbon interferences such as vegetable and animal oils and greases, organic acids, chlorinated hydrocarbons, phenols and phthalate esters will also be measured. The presence of petroleum hydrocarbons in TRH may be confirmed by clean-up of the extract with silica gel. However, silica gel clean-up may not completely remove non-petroleum hydrocarbon interferences of biological origin.

10.2.8.2 Sample Extraction

The table below lists the specified US EPA SW-846 methods.

3540C	Soxhlet extraction using: dichloromethane/acetone (1:1).
3550C	Ultrasonic extraction* using: dichloromethane/acetone (1:1)
3545A	Pressurised fluid extraction (PFE) using: dichloromethane/acetone (1:1) or hexane/acetone (1:1).
CRC CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking using: dichloromethane/acetone (1:1) This procedure, specified for TRH, has evolved from work carried out by CRC CARE (2009). Although all components of it are in common use, no validation data are currently available for the entire method.

* Ensure samples do not overheat.

The solvent system chosen should be shown to give optimum, reproducible recovery of analytes spiked into the particular matrix (soil type) under test.

10.2.8.3 Extract clean-up

(Recommended when there is significant amount of non-petroleum hydrocarbon interferences, to avoid reporting false positive results.)

The table below lists the specified US EPA SW-846 methods.

3630C	Silica gel clean-up
	Clean-up is necessary if the extract contains interfering quantities of polar non-petroleum compounds evidenced by a GC/FID profile or GC/MS analysis uncharacteristic of petroleum hydrocarbons.
	Clean-up may be achieved after solvent exchange to hexane or other suitable solvent. Clean-up can be either carried out using a silica gel column or by shaking a solvent extract with loose silica gel.
	Silica gel activity may have to be adjusted by water addition for optimum retention of PAHs and TRH in the extract. US EPA Method 3630C gives conditions for silica gel clean-up of PAHs.

10.2.8.4 Extract Analysis

The table below lists the specified US EPA SW-846 methods.

8015B	Specifies GC/FID conditions up to nC28 alkanes
	GC/FID conditions for >nC28 alkanes can be obtained from 8270D or in Appendix 1 (CRC CARE method).
	Due to the non-specific response of GC/FID, identities of unusual mixtures and predominant individual compounds should be confirmed using GC/MS.
	TRH fractions are specified as >C ₁₀ -C ₁₆ , >C ₁₆ -C ₃₄ and >C ₃₄ -C ₄₀ .

	<p>Details of GC conditions, standards, and procedure for quantification of fractions are listed in Appendix 1.</p> <p>Where clean-up with silica gel has occurred it should be clearly stated on the report. The result will be reported as TRH–silica.</p>
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10.2.9 Phenols

10.2.9.1 Scope and application

This method is applicable but not limited to the analysis of the following phenolic compounds:

- Phenols
- Chlorophenols, Dichlorophenols, Trichlorophenols
- Tetrachlorophenols, Pentachlorophenol
- Cresols (methyl phenols)
- Nitrophenols, Dinitrophenols

10.2.9.2 Sample extraction

The table below lists the specified US EPA SW-846 methods.

3540C	<p>Soxhlet extraction using: acetone/hexane (1:1) or dichloromethane/acetone (1:1) plus exchange solvent (2-propanol).</p>
3545A 3550C	<p>Pressurised fluid extraction (PFE)</p> <p>Ultrasonic extraction* using:</p> <p>a. for low concentration (individual compounds <20 mg/kg): dichloromethane or dichloromethane/acetone (1:1) or hexane/acetone (1:1) or methyl tertiary-butyl ether or methyl tertiary-butyl ether/methanol (2:1) and exchange solvent (2-propanol).</p> <p>The solvent system chosen should be shown to give satisfactory, reproducible recovery of analytes spiked into the particular matrix (soil type) under test.</p> <p>Analysts should determine an appropriate concentration limit and ensure that quantitative results are based on sample concentrations that do not exceed the instrumental range.</p> <p>b. for high concentration (individual compounds >20 mg/kg): dichloromethane.</p>

* Ensure samples do not overheat.

CRC CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking.
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10.2.9.3 Extract clean-up

The tables below list the specified US EPA SW-846 methods.

3630C	Silica gel column clean-up (for samples derived for GC/ ECD determination).
3640A	Gel permeation clean-up
3650B	Acid/base partition extraction (it is recommended that all extracts undergo this clean-up): pentafluorobenzyl bromide derivatisation (for GC/ECD analysis) phenols by GC/capillary column technique

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	8041A	GC/FID GC/ECD (after derivatisation, if interferences prohibit proper analysis by GC/FID)
(P)	8270D	GC/MS

Note: GC analysis of some un-derived phenols is difficult (e.g. chlorinated and nitro compounds). The GC injector port should be clean and adequately silanised.

10.2.10 Chlorinated herbicides

10.2.10.1 Scope and application

The method described below for chlorinated herbicides (by gas chromatography) is applicable but not limited to the determination of:

2,4-D	DCPA diacid	5-Hydroxydicamba
2,4-DB	Dalapon	MCPA
2,4,5-T	Dicamba	MCPP (mecoprop)
2,4,5-TP (Silvex)	3,5-Dichlorobenzoic acid	Pentachlorophenol
Acifluoren	Dichlorprop	Picloram
Chloramben	Dinoseb	

10.2.10.2 Sample extraction

The tables below list the specified US EPA SW-846 methods.

8151A	The soil is extracted and may be derived with diazomethane or 2,3,4,5,6-pentafluorobenzyl bromide.
3545A	Pressurised fluid extraction (PFE)

10.2.10.3 Extract clean-up

3650B	Acid/base partitioning step if required
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10.2.10.4 Extract analysis

8151A	GC/ECD
8270D	GC/MS

10.2.10.5 Extract analysis

8151A	GC/ECD
8270D	GC/MS

10.2.11 Phthalate esters

10.2.11.1 Scope and application

This method is applicable but not limited to analysis of the following phthalate esters:

Bis (2-n-butoxyethyl) phthalate	Dicyclohexyl phthalate
Bis (2-ethoxyethyl) phthalate	Diethyl phthalate
Bis (2-ethylhexyl) phthalate	Dihexyl phthalate
Bis (2-methoxyethyl) phthalate	Diisobutyl phthalate
Bis (4-methyl-2-pentyl) phthalate	Dimethyl phthalate
Butyl benzyl phthalate	Dinonyl phthalate
Diamyl phthalate	Di-n-octyl phthalate
Di-n-butyl phthalate	Hexyl 2-ethylhexyl phthalate

10.2.11.2 Sample extraction

The table below lists the specified US EPA SW-846 methods.

3545A	Pressurised fluid extraction (PFE)
3540C	Soxhlet extraction using: acetone/hexane (1:1) or dichloromethane/acetone (1:1).
3550C	Ultrasonic extraction* using: a. for low concentration (individual compounds <20 mg/kg): dichloromethane or dichloromethane/acetone (1:1) or hexane/acetone (1:1) or methyl tertiary-butyl ether or methyl tertiary-butyl ether/methanol (2:1). The solvent system chosen should be shown to give satisfactory, reproducible recovery of analytes spiked into the particular matrix (soil type) under test. Analysts should determine an appropriate concentration limit and ensure that results are based on sample concentrations that do not exceed the

	instrumental range. b. for high concentration (individual compounds >20 mg/kg): dichloromethane or hexane.
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* Ensure samples do not overheat.

CRC CARE TPH TECHNICAL WORKING GROUP	End-over-end tumbling/shaking
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10.2.11.3 Extract clean-up

Note: The analyst should verify that quantitative recovery of phthalates is achieved for whichever clean-up procedure used.

The tables below list the specified US EPA SW-846 methods.

3620C	Florisil® column clean-up
3640A	Gel-permeation clean-up

10.2.11.4 Extract analysis

8061A	GC/ECD
8270D	GC/MS

10.2.12 Dioxins and furans

10.2.12.1 Scope and application

This method is applicable but not limited to the analysis of the following PCDDs and PCDFs by high resolution gas chromatography/low resolution mass spectrometry (HRGC/LRMS), or HRGC/high resolution mass spectrometry (HRMS):

- 2,3,7,8 tetrachloro dibenzo-p-dioxin
- 2,3,7,8 tetrachloro dibenzofuran.

10.2.12.2 Sample extraction

The tables below list the specified US EPA SW-846 methods.

3545A	Pressurised fluid extraction (PFE)
3546	Microwave extraction using hexane: acetone (1:1)
8290A	Soxhlet and Dean-Stark separator extraction using toluene (a) for low concentration (individual compounds (<1 µg/kg): toluene
8280B	Soxhlet and Dean-Stark separator extraction using toluene (b) for high concentration (individual compounds (>1 µg/kg): toluene

10.2.12.3 Extract clean-up

Methods for the clean-up of some co-extracts/analytes are suggested below.

8280B	Acid/base clean-up followed by: silica gel column clean-up alumina clean-up carbon clean-up.
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Note: Acid/base clean-up may not be necessary for uncoloured extracts.

10.2.12.4 Extract analysis

8280B	PCDDs and PCDFs by HRGC/LRMS. This method applies to reporting of total concentration of TCDD/PCDF in a given level of chlorination. Complete chromatographic separation of all 210 isomers is not possible under stated instrumental conditions. Quantification limits are greater than 1 µg/kg of solid (parts per billion).
8290A	PCDDs and PCDFs by HRGC/HRMS. This method applies to reporting individual concentration of tetra- through to octa-chlorinated TCDD/PCDF homologues. Quantification limits are less than 1 µg/kg of solid (parts per billion). Sensitivity of method is dependent on level of interference in matrix.
1613B	Isotope dilution. High resolution GC/MS.

11 Leachable contaminants

11.1 Scope and application

The leachability characteristics of a contaminant can be used to help predict the likely impact it will have if the soil is left on site, proposed for re-use or intended for disposal.

Contaminants in soil can leach into groundwater under certain conditions, depending on the local chemistry and geology of a site—leachability is particularly affected by soil pH, contaminant solubility and Redox conditions. These parameters are not controlled in leaching tests but should be recorded from field tests, and other laboratory tests, to ensure that leachability test results can be evaluated accordingly.

A variety of leaching tests are available, and it is important to specifically test leachability in soil under conditions approximating those found in the field or the proposed end-use environment.

Leachability testing can be of two types:

- batch leaching (or static extraction tests) – equilibrium based
- dynamic leaching – column and diffusion tests.

Generally, batch tests have a much shorter duration than dynamic tests though the latter may give a better representation of contaminant leaching. Batch extraction protocols assume that a steady-state condition is achieved by the end of the test.

All methods are designed to simulate leaching conditions in the environment and thus estimate the likely availability of contaminants. The choice of leaching reagent should be based on the environmental conditions to which the soil or wastes are likely to be exposed — ideally using actual surface and groundwater from the relevant site.

The two most relevant leaching tests for Australian conditions are:

- Australian standard leaching procedure (ASLP) as per Australian standards 4439.1 (AS4439.1-1999), 4439.2 (AS 4439.2-1997) and 4439.3 (AS 4439.3-1997)
- toxicity characteristic leaching procedure (TCLP) as per US EPA method 1311, (US EPA SW846, Method 1311).

The ASLP allows a wide range of leaching reagents to be used and is generally the most appropriate leach test to cover a range of conditions encountered in contaminated site management in Australia, whether soil is to remain on site or be moved.

The exception is where contaminated soil is to be disposed of at a municipal landfill and mixed with municipal solid waste (MSW), in which case TCLP is more appropriate.

The TCLP was designed to simulate conditions in a MSW landfill. It is not suitable for soil that is NOT intended to be mixed with MSW.

Leachable organics (volatile and semi-volatile), metals and anions (except cyanide) may be determined using ASLP (or TCLP if permitted by local regulatory guidelines). The zero headspace methods for ASLP (AS 4439.2-1997) and TCLP (US EPA SW-846, Method 1311) list the volatile compounds of concern. The ASLP procedure lists an informative group of volatile compounds, but does not preclude others. The TCLP (US EPA SW-846, Method 1311) lists benzene, carbon tetrachloride, chlorobenzene, chloroform, 1,2-dichloroethane, 1,1-dichloroethylene, methyl ethyl ketone, tetrachloroethylene and vinyl chloride as toxicity characteristic constituents at a contaminated site.

Leachable cyanide may be determined by the synthetic precipitation leaching procedure (US EPA SW-846, Method 1312) using deionised water leach fluid or by the ASLP methods described in AS 4439.2-1997, also using distilled or deionised water as the leach fluid.

Leachates collected from the leaching procedures should be analysed using methods listed for waters and wastewaters.

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13 Appendix 1: Determination of total recoverable hydrocarbons (TRH) in soil

This material has been adapted from procedures developed by the CRC CARE TPH Technical Working Group, convened by CRC CARE in 2009. References used include:

- CRC CARE 2009, *Health screening levels for petroleum hydrocarbons in soil and groundwater*, CRC CARE TPH Technical Working Group, Cooperative Research Centre for Contamination Assessment & Remediation of Environment, Adelaide, Australia.
- US EPA 1999, Method 1664: *n-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated n-Hexane Extractable Material (SGTHEM; Non-polar Material) by Extraction and Gravimetry*, Revision A, US EPA Office of Water, United States Environment Protection Authority.

13.1 Volatile (C₆ - C₁₀) and semi-volatile (>C₁₀-C₄₀) TRH

These methods can be used to determine TRHs in soil by gas chromatography with an appropriate detector. The term 'TRH' is equivalent to the historically reported 'TPH'.

Method A1 can determine volatile TRH (vTRH) and can be used to investigate sites contaminated with petrol, other light fuels and petroleum-based solvents.

Method A2 can determine semi-volatile TRH and can be used to investigate sites contaminated with diesel, other petroleum fuels, mineral oil and petroleum-based solvents.

The methods are performance-based and designed to be rapid and economical. To obtain consistent and reliable results, they should be carried out by experienced analysts trained in the operation, maintenance and troubleshooting of GC instrumentation and in interpretation of gas chromatograms.

This section describes the general principles common to both methods, including quality control and method validation procedures.

The term 'TRH—total recoverable hydrocarbons' should be used when referring to data generated using these test methods where no clean-up is employed.

If silica clean-up is employed, the results should be qualified as 'TRH—silica'.

13.1.1 Quality control considerations

Standard quality controls are required to ensure the correct performance of these methods (see Section 4). Quality control measures should include a calibration verification standard (CVS)—consisting of a hydrocarbon product mix—and a laboratory control sample (LCS)—consisting of a suitable hydrocarbon product mix. Ideally, the LCS should be spiked with hydrocarbons that test all fractions reported.

Calibration verification standard (CVS) – A known quantity of hydrocarbon product(s) is/are dissolved in extraction solvent. This standard should contain hydrocarbons covering the required hydrocarbon fractions being analysed and serves as a check on the GC system and quantification procedure. The CVS should be between 80 and 120% of the expected concentration in the sample. This can be run once per sequence or 24 hour period.

Laboratory control sample (LCS) – As a minimum, a laboratory control sample should be run with each batch of 20 samples. This quality control sample should be processed through the entire analytical method and reported with the data. The LCS is a clean soil fortified with the same hydrocarbon product mix as used for the CVS, or a reference sample with a consensus hydrocarbon value. Recovery of product should be checked by analysing either ethanol-free petrol or any other

suitable product with predominant hydrocarbons in the nC₆– nC₁₀ range. The calculated LCS concentration should be between 70 and 130% of the expected concentration or a recovery range established by ongoing quality control charts.

13.1.2 Method validation

The methods should be validated by each laboratory using them, in accord with this Schedule. Some method validation parameters require particular attention, as below.

13.1.2.1 Hydrocarbon product linearity

Establish linearity of the detector response using hydrocarbon products that cover the particular hydrocarbon fraction (for example, ethanol-free petrol for Method A1 (analysis of volatiles), or a mix of diesel and motor oil for Method A2, (analysis of semi-volatiles). Linearity should be within 15% in each of the calibrated carbon ranges. As a general principle, the peak height of the largest product component in a fraction should not exceed the peak height of the single n-alkane in the highest level calibration standard.

13.1.2.2 Product standard reference materials

A reference hydrocarbon product(s) should be prepared and analysed. The product(s) should cover the range of hydrocarbon fractions specified in this method. The product or products should be well characterised, such that the quantitative composition of the relevant fractions is known. This allows the assignment of a portion of a known quantity of this product to a particular fraction. This solution can then be ideally used as the CVS for ongoing quality control.

Accuracy of the method should be established by obtaining acceptable recoveries for hydrocarbons from a certified reference material (i.e. soil contaminated with hydrocarbons).

13.1.2.3 Proficiency studies

Ongoing participation in relevant proficiency studies is required to validate this method.

13.2 Method A1: Determination of volatile TRH: TRH C₆ – C₁₀

13.2.1 Scope and application

This method is applicable to the determination of hydrocarbons eluting between nC₆ and nC₁₀ alkanes, inclusive of BTEX. Target compound analysis can occur simultaneously when running this method, provided that suitable specific detectors are employed, e.g. PID for aromatic compounds, or MS.

Note: Semi-volatile hydrocarbons with higher boiling points should be analysed by the TRH semi-volatile method (see Method A2 below (Section 14.3) and Section 11.13).

13.2.2 Limitations

- This method does not distinguish between petrogenic and biogenic compounds or synthetic compounds, such as chlorinated solvents; it measures the *total* recoverable hydrocarbons present, hence it is designated TRH.
- Excess moisture in sample: the method requires extraction of the sample with methanol, which is soluble in water. Excess moisture can dilute the extraction solvent, increasing the solvent volume thus diluting the extract.
- High organic carbon content in sample: methanol is a relatively weak solvent for non-polar compounds. Volatile analytes may be retained by matrices containing high organic carbon levels. Surrogates added to extractions may preferably partition onto the carbon matrix.

13.2.3 Interferences

The method is subject to certain interferences including:

- highly contaminated samples may cause a carry-over on the instrument
- laboratory background, including ambient air, carry-over and contaminated soils.

13.2.4 Principle

A soil sample (>5 g) is extracted with a sufficient volume of methanol, then the methanol is separated from the soil and added to a purging vessel or other equivalent apparatus for determination of volatile compounds, using FID or MS in scan mode.

13.2.5 Method

13.2.5.1 Apparatus

A gas chromatograph with appropriate detector for hydrocarbon determination. Columns suitable for volatiles, as specified in US EPA Method 8260B (latest version).

13.2.5.2 Reagents and standards

Reagents

Unless otherwise specified, all reagents shall be of analytical grade (AR) and all solvents of chromatography grade. Chromatography grade methanol and organic-free water are recommended, and ultra-pure carrier gas for gas chromatography.

Standards

Internal standard

This solution comprises a suitable compound dissolved in methanol to a suggested concentration of 10 mg/L and should be stored at 4°C. Suitable compounds are specified in US EPA Method 8260B.

Surrogate standard

This standard comprises a methanol solution containing at least one surrogate compound. Suitable compounds include 4-bromofluorobenzene, dibromofluoromethane, toluene-d₈. It should be stored at 4°C.

Calibration standard solutions

nC₆–nC₁₀ TRH Standard (standards for mass selective detector or flame ionisation detector).

Owing to the differential responses of mass spectrometric detectors towards aliphatic and aromatic compounds, it is essential that the standard contains representatives of both groups.

This standard should therefore consist of about 40% aromatic and 60% aliphatic target analytes, in order to be representative of a typical Australian fuel. The aromatic compounds shall comprise the components of BTEX. The aliphatics shall comprise equal proportions of all n-alkanes in the C₆–C₁₀ range.

These solutions are stable for 6 months when stored at ≤6°C with minimum headspace and away from all possible sources of contamination.

Note: If a different fraction split is requested, the relevant compounds shall be represented in the calibration standard solution.

While it may be possible to store and use the stock solutions for longer than 12 months after preparation, the laboratory should assure itself of the stability of the solution by carrying out regular checks of the concentration of the analyte. The laboratory should retain records to confirm the stability of the solutions.

Calibration verification standard solution

Calibration performance should be assessed against ethanol-free petrol or any other suitable product with predominant hydrocarbons in the nC_6 – nC_{10} range used to check validity of the calibration curve.

The product should be well characterised, such that the quantitative composition of the relevant fractions is known. This allows the assignment of a portion of a known quantity of this product to a particular fraction.

Calibration standards

Initial calibration

This involves analysis of at least five different concentrations covering the working range of the instrument used. Extrapolation of the response curve above the highest calibration level is not recommended. Initial calibration is run at the beginning of each analytical sequence.

13.2.5.3 Procedure

1. Open the sample jar quickly, scrape off the top 1 cm of sample and discard. Remove all extraneous material (grass, pebbles, etc.) from the sample. Obtain the subsample by driving an inert coring device (PTFE or stainless steel spatula) into the sample and rapidly transfer a minimum of 5 g into a tared extraction vessel. Record the weight.
2. Add methanol (at a minimum ratio of 1:2 sample:solvent) and an appropriate amount of surrogate standard solution in order to produce a final surrogate concentration at about the midpoint of the calibration range, taking further dilutions into consideration.
3. Shake extract for about 30 minutes using end-over-end tumbler, orbital shaker or ultrasonic bath. Allow to settle. Clay samples should be completely disintegrated before an aliquot is taken for analysis. Samples should be maintained in a cool environment to ensure they do not overheat.
4. Analyse an aliquot of methanol extract using an appropriate instrument for hydrocarbon analysis. If an internal standard is used, it should be included with the methanol extract transfer. Alternatively, the internal standard may be added automatically by instruments having this capability.

13.2.6 GC Analysis

13.2.6.1 Calibration

At least five calibration standards should be prepared from the relevant calibration standard solution.

- The calibration curve should have a linear regression of >0.99
- At a minimum, run a daily check of the lowest calibration standard and the midpoint calibration standard to confirm stability of the calibration curve. Rerun the calibration curve if the low standard deviates by more than 30% from the curve or if the midpoint calibration standard deviates by more than 20% from the curve.
- A CVS is run to check the validity of the calibration curve against a characterised hydrocarbon product.

13.2.6.2 Measurement of test sample

After calibration, carry out the determination on the test samples (field or laboratory methanol extracts). Where the analyst has some prior knowledge regarding the relative concentration of analytes in the samples, the run should be arranged in order of increasing concentration. In the absence of such information and if samples with high concentration of analytes occur in the middle of a run, the analyst should examine the analytical run for possible carry-over, and re-analyse affected samples, if required.

13.2.7 Calculations

13.2.7.1 Integration of peaks

All peaks in a chromatogram should be integrated and included in the calculation of results. The total area contributed by the surrogate and internal standards should be excluded from the calculation of the final result.

13.2.7.2 Calculation of *v*TRH ($C_6 - C_{10}$) content

Integrate the appropriate chromatogram.

The C_6-C_{10} fraction is integrated from the peak start of the nC_6 peak to the time corresponding to the end of the nC_{10} peak.

The *v*TRH content is calculated according to the following formula:

$$C = \frac{\text{Area of C in sample} \times I_{STD} \times \text{conc. of standard} \times VF \times ME \times 100}{I_{SAM} \times \text{Area of standard} \times MA \times W \times (100 - \% \text{ moisture})}$$

where:

<i>C</i>	=	<i>v</i> TRH in soil (mg/kg)
<i>VF</i>	=	Volume of water-methanol extract as analysed by purge and trap (L)
<i>MA</i>	=	Volume of methanol extract transferred into reagent water (L)
<i>ME</i>	=	Volume of methanol added to soil/sediment (L)
<i>W</i>	=	Weight of soil/sediment analysed (kg)
<i>I</i> _{STD}	=	Peak area or height produced by internal standard in calibration chromatogram
<i>I</i> _{SAM}	=	Peak area or height produced by internal standard in sample chromatogram
% Moisture	=	Moisture content of original soil/sediment expressed as % w/w

The method blank should contain no detectable levels of analytes of interest and results of the method blank should not be subtracted from sample results.

13.3 Method A2: Determination of semi-volatile TRH: TRH >C₁₀ - C₄₀

13.3.1 Scope and application

The method is applicable to the determination of hydrocarbons eluting between $>nC_{10}$ and nC_{40} alkanes. The method extracts target component hydrocarbons such as PAHs. If the presence of PAHs is suspected, target analysis techniques are preferred for risk assessments. Volatile hydrocarbons with lower boiling points than nC_{10} or heavy petroleum products (boiling points $>nC_{40}$) will not be quantitatively determined using this method.

Where significant levels of non-TPH interferences are suspected, a silica gel clean-up procedure is included as an optional but recommended clean-up step (with the results qualified as 'TRH-silica').

13.3.2 Limitations

The method cannot be used to provide quantitative data for the nC₆ to nC₁₀ hydrocarbon range, as it allows loss of the most volatile components in the sample, mainly during the weighing and chemical drying steps. For quantitative analysis of nC₆ to nC₁₀ hydrocarbons, refer to Method A1 in this Schedule.

13.3.3 Interferences

Interferences may be caused by any organic compounds that are soluble in the extracting solvent and that elute from the GC under the conditions used. These may include vegetable and animal oils and fats, chlorinated and other solvents, plasticisers, etc. The use of silica to adsorb polar compounds may reduce these interferences.

Impurities in the extracting solvent, drying agents and silica will interfere, and can be reduced by the use of high purity solvents. Laboratory blanks should be analysed with each batch of samples.

Carry-over from previous highly contaminated samples extracted in the same glassware may cause spurious elevated results, which can be minimised through efficient cleaning of all glassware, syringes, etc.

13.3.4 Principle

A soil sample (>10 g) is treated with anhydrous sodium sulfate then extracted into a minimum of 20 mL 1:1 DCM:acetone. The sample is extracted by mechanical end-over-end shaking for a minimum of 1 hour or other suitably validated extraction techniques (ASE[®], horn probe ultrasonication, mechanical wrist action shaker or soxhlet extraction). Where non-TPH interferences are suspected, a silica gel treatment step is recommended.

The extract is analysed with a phenyl polymethylsiloxane phase column containing up to 5% polymethylsiloxane using a GC equipped with an FID. The results are reported as the amount of hydrocarbon in three defined fractions – >nC₁₀–nC₁₆, >nC₁₆–nC₃₄ and >nC₃₄–nC₄₀.

13.3.5 Method

13.3.5.1 Apparatus

- Gas chromatograph with FID
- Column: non-polar or semi-polar bonded phase capillary column is strongly recommended (polymethylsiloxane up to 5% phenyl polymethylsiloxane)
- Integrator or computer and integration software
- Volumetric pipettes and glassware—they should all be regularly calibrated and a calibration record maintained.

13.3.5.2 Reagents and standards

Reagents

All reagents used in this method should be reagent grade or higher.

Dichloromethane (DCM) and acetone should be high purity and give no interference peaks by GC-FID.

Anhydrous sodium sulfate may contain plasticisers leached from plastic storage containers;

each batch should be checked before use. A suggested clean-up method is as follows:

1. Spread the sodium sulfate on a metal tray to a depth of <2 cm.
2. Ignite in a muffle furnace at 600°C for 1 hour.
3. Cool and store in a sealed metal or glass container.

Silica (e.g. Merck, Silica Gel 60, 70–230 mesh, methods may require a specific mesh size)

Should be appropriately activated to meet the performance requirements of the method. For example, dry at 200–250°C for 24 hours minimum and store in a desiccator or tightly sealed container. Deactivate by adding an appropriate weight of reagent grade water and mix thoroughly.

Note: degree of deactivation depends on the constitution of the solvent extract to be cleaned up.

Calibration standards

- The fraction definition standards for this method—and the calibration standards used to quantify the fractions—are nC₁₀, nC₁₆, nC₃₄ and nC₄₀.
- A calibration verification standard consists of hydrocarbon product dissolved in extraction solvent. Products used as calibration verification mixes should cover the applicable carbon ranges of the method.
- Freshly made calibration standards should be checked by GC–FID against the calibration standards currently being used in the TRH method as a check for any gross error in their preparation.

13.3.5.3 Procedure

- Weigh a minimum of 10 g of sample into a tared vessel.
- Add sufficient amount of anhydrous sodium sulfate to permit drying of sample.
- Add a minimum of 20 mL DCM:acetone (1:1) and extract by end-over-end tumbler for a minimum of 1 hour. Alternative extraction solvent mixes or extraction procedures can be used if results meet method performance criteria.

13.3.5.4 Silica gel clean-up

Quantities of silica gel used will vary with the volume of extract and the suspected concentration of polar substances. The choice of solvent and suitably deactivated silica gel should demonstrate a quantitative recovery of aliphatic and aromatic hydrocarbons of between 70 and 130%. When validating a particular procedure, this should be demonstrated to quantitatively remove a typical surrogate polar compound, for example, palmitic or stearic acid.

The procedure described below is for a dispersive sorbent clean-up. Mini-columns or commercial silica solid phase cartridges (SPC) may also be used if comparable method performance criteria can be met.

- Exchange an aliquot of sample extract into a suitable solvent for clean-up. For example, a 1:1 DCM:acetone extract should be exchanged into a solvent other than acetone, to allow for removal of polar substances.
- To the solvent-exchanged extract add an appropriate weight of silica gel. If an empirical determination of bulk density has been made, the weight may be replaced with an appropriate volume.
- Mix the extract and silica gel thoroughly (e.g. with a vortex mixer) and allow the sorbent to settle before removing a portion of the extract for analysis.

US EPA 3630C silica clean-up method gives information about clean-up of PAHs, PCBs, OCs and phenols but not specifically for hydrocarbons. On the other hand, US EPA Method 1664 gives silica gel clean-up information specifically for hydrocarbons.

Limitations

1. Silica gel has a capacity to adsorb polar compounds, at approximately 30 mg per gram of material. Silica may become overloaded if too much polar material is present beyond the capacity of silica gel used. In such cases, multiple clean-up steps may be required.
2. Waste sludges containing paint can give anomalous results due to clean-up procedures being unable to remove all such unwanted material. Such non-polar polymeric materials remaining in a solvent extract can then degrade in the high temperature GC injector, producing smaller hydrocarbon molecules recorded as petroleum hydrocarbons. In such situations, alternate clean-up procedures should be investigated, for example, gel permeation chromatography (GPC).
3. Soils high in organic matter may also give false positive results.

13.3.6 GC analysis

The sample should be analysed using a gas chromatograph fitted with an FID.

13.3.6.1 GC conditions

The exact conditions used will vary from laboratory to laboratory.

Injector: a split/splitless injector at >250°C is recommended. The injection liner should be checked and replaced regularly.

Oven: the oven ramp should be a single linear ramp. The final temperature of the oven program should be as high as possible to ensure maximum removal of the higher molecular weight hydrocarbons from the column prior to the next analysis.

Column: the capillary column should be a non-polar to semipolar phase—such as a bonded phase of polydimethylsiloxane containing up to 5% phenyl polydimethylsiloxane.

13.3.6.2 Chromatographic integration

The sample sequence should have adequate solvent blanks run to monitor baseline drift. Samples are integrated by taking a horizontal line from a baseline point after the elution of nC₁₀. The fraction areas are calculated by the software and concentrations determined according to the ‘Calculations’ section below.

13.3.6.3 GC calibration

Perform calibration and retention time marking for the nC₁₀ to nC₄₀ hydrocarbons using approximately equal weights of nC₁₀, nC₁₆, nC₃₄ and nC₄₀ hydrocarbons dissolved in hexane (toluene can be added to assist dissolution).

- At a minimum, run a 5-point calibration curve using the nC₁₄, nC₂₄ and nC₃₆ hydrocarbons and a blank before analysis begins. Linearity should have a linear regression of >0.99.
- At a minimum, run a daily check of the lowest calibration standard and the midpoint calibration standard to confirm stability of the calibration curve. Rerun the calibration curve if the low standard deviates by more than 30% from the curve or if the midpoint calibration standard deviates by more than 20% from the curve.

13.3.7 Calculations

Calculation of TRH fractions in a sample:

$$>C_{10}-C_{16} \text{ hydrocarbons (mg/kg)} = \frac{A_{>C_{10}-C_{16}} \times C_{14 \text{ conc}} \times \text{Vol}_{\text{ext}} \times F \times 100}{A_{C_{14}} \times W \times \%DW}$$

$$>C_{16}-C_{34} \text{ hydrocarbons (mg/kg)} = \frac{A_{>C_{16}-C_{34}} \times C_{24 \text{ conc}} \times \text{Vol}_{\text{ext}} \times F \times 100}{A_{C_{24}} \times W \times \%DW}$$

$$>C_{34}-C_{40} \text{ hydrocarbons (mg/kg)} = \frac{A_{>C_{34}-C_{40}} \times C_{36 \text{ conc}} \times \text{Vol}_{\text{ext}} \times F \times 100}{A_{C_{36}} \times W \times \%DW}$$

where:

$A_{>C_{10}-C_{16}}$ = the integration of all area counts from the end of the nC_{10} to the end of the nC_{16} peak

$A_{>C_{16}-C_{34}}$ = the integration of all area counts from the end of the nC_{16} to the end of the nC_{34} peak

$A_{>C_{34}-C_{40}}$ = the integration of all area counts from the end of the nC_{34} to the end of the nC_{40} peak

C_{14} = concentration of C_{14} standard (mg/litre)

C_{24} = concentration of C_{24} standard (mg/litre)

C_{36} = concentration of C_{36} standard (mg/litre)

Vol_{ext} = Final volume of sample extract (litre)

F = Dilution factor applied to bring the samples and standards into appropriate peak height range

W = weight of sample taken (kg)

$\% DW$ = % Dry weight

14 Shortened forms

ABC	ambient background concentration
ACL	added contaminant limits
ADWG	<i>Australian drinking water guidelines</i>
AM	arithmetic mean
ANCE	excess acid neutralizing capacity
APHA	American Public Health Association
AS	Australian Standard
ASE©	accelerated solvent extractor
ASLP	Australian standard leaching procedure
ASTM	American Society for Testing & Materials
AWQG	<i>Australian and New Zealand guidelines for fresh and marine water quality</i>
BTEX	benzene, toluene, ethylbenzene and xylenes
CEC	cation exchange capacity
CI	confidence interval
CL	confidence limit
CRC CARE	Cooperative Research Centre for Contamination Assessment and Remediation of the Environment
CRM	certified reference material
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CVS	calibration verification standard
CWS PHC	<i>Canada Wide Standard for Petroleum Hydrocarbons (PHCs) in Soil</i>
DQO	data quality objective
EIL	ecological investigation level
ESL	ecological screening level
FA	fibrous asbestos
FID	flame ionisation detector
GC	gas chromatography
GC/ECD	GC/electron capture detector
GC/ELCD	GC/ electrolytic conductivity detector
GC/FID	GC/flame-ionisation detector
GC/FPD	GC/flame photometric detector
GC/MCD	GC/microcoulometric detector
GC/MS	GC/mass spectrometry
GC/NPD	GC/nitrogen-phosphorus (thermionic) detector
GC/PID	GC/photo-ionisation detector
GIL	groundwater investigation level
GM	geometric mean
GMRRW	<i>Guidelines for managing risk in recreational water</i>
HEM	n-Hexane extractable material
HIL	health investigation level
HPLC	high-performance liquid chromatography
HPLC/ECD	HPLC/electrochemical detector
HPLC/F	HPLC/fluorescence detector
HPLC/MS	HPLC/mass spectrometry
HPLC/UV	HPLC/ ultraviolet detector
HRGC/HRMS	high-resolution gas chromatography/high-resolution mass

HRGC/LRMS	spectrometry high-resolution gas chromatography/low-resolution mass spectrometry
HSL	health screening level
ICV	independent calibration verification
IEUBK	Integrated exposure uptake biokinetic model (for lead)
ISO	International Standards Organisation
ISQG	<i>Interim sediment quality guideline</i>
KD	Kuderna-Danish evaporator
LCS	Laboratory Control Sample
LNAPL	light non-aqueous phase liquid
LOD	limit of detection
LOEC	lowest observed effect concentration
LOR	limit of reporting
MAH	monocyclic aromatic hydrocarbon
MDL	method detection limit
MS	mass spectrometry
MSW	municipal solid waste
MU	Uncertainty of Measurement
NATA	National Association of Testing Authorities, Australia
NL	non limiting
NMI	National Measurement Institute
NMR	nuclear magnetic resonance
OCP	organochlorine pesticides
OPP	organophosphorus pesticides
(P)	preferred method
PAHs	polycyclic aromatic hydrocarbons
PCBs	polychlorinated biphenyl compounds
PFE	pressurised fluid extraction
pHox	peroxide pH
PID	photo ionisation detector
PQL	practical quantification limit
PTA	Proficiency Testing Australia
PTFE	polytetrafluoroethylene
QA	quality assurance
QC	quality control
RPD	relative percent difference
RRT	relative retention time
RSD	relative standard deviation
RT	retention time
SD	standard deviation
SFE	supercritical fluid extraction
SGT-HEM	silica gel treated n-hexane extractable material
SPC	solid phase cartridge
SRM	standard reference material
SVOC	semi-volatile organic compounds
TAA	titratable actual acidity
TCLP	toxicity characteristic leaching procedure
TDS	total dissolved solids
TEF	toxicity equivalence factor
TEQ	toxicity equivalent quotient

TOC	total organic carbon
TPA	titratable peroxide acidity
TPH	total petroleum hydrocarbons
TRH	total recoverable hydrocarbons
TRH-silica	total recoverable hydrocarbons - silica gel clean-up employed
UCL	upper confidence limit
US EPA	United States Environmental Protection Agency
VHC	volatile hydrocarbons
VOA	volatile organic analysis
VOCC	volatile organic chlorinated compound
vTRH	volatile total recoverable hydrocarbons
WAD	weak acid dissociable cyanide
WHO	World Health Organization